

AD-A229 296

# The Use of Solid Ceramic and Ceramic Hard-Coated Components to Prolong the Performance of Perfluoropolyalkylether Lubricants

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30 September 1990

Prepared for  
SPACE SYSTEMS DIVISION  
AIR FORCE SYSTEMS COMMAND  
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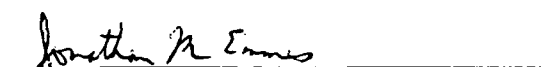
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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-88-C-0089 with the Space Systems Division, P.O. Box 92960, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by J. M. Straus, Director, Chemistry and Physics Laboratory. Lt Borden was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) Program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <u>Unclassified</u>			1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT  Approved for public release; distribution unlimited.			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S) SSD-TR-90-32			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) TR-0090(5945-03)-2			7a. NAME OF MONITORING ORGANIZATION Space Systems Division			
6a. NAME OF PERFORMING ORGANIZATION The Aerospace Corporation Laboratory Operations		6b. OFFICE SYMBOL (If applicable)		7b. ADDRESS (City, State, and ZIP Code) Los Angeles Air Force Base Los Angeles, CA 90009-2960		
6c. ADDRESS (City, State, and ZIP Code) El Segundo, CA 90245-4691		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F04701-88-C-0089				
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)		10. SOURCE OF FUNDING NUMBERS		
8c. ADDRESS (City, State, and ZIP Code)		PROGRAM ELEMENT NO.		PROJECT NO.	TASK NO.	
				WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) The Use of Solid Ceramic and Ceramic Hard-Coated Components to Prolong the Performance of Perfluoropolyalkylether Lubricants						
12. PERSONAL AUTHOR(S) Carré, David J.						
13a. TYPE OF REPORT		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 1990 September 30		
				15. PAGE COUNT 20		
16. SUPPLEMENTARY NOTATION						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
FIELD	GROUP	SUB-GROUP	Ceramics Perfluoropolyalkylether oil Wear testing			
			Hard coatings Silicon Nitride			
			Lubricants Titanium nitride			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  The performance of perfluoropolyalkylether (PFPE) oils under boundary lubrication conditions was tested using 440C stainless steel, silicon nitride/440C hybrid, and titanium nitride hard-coated ball-bearing components. By limiting the chemical interactions between the lubricant and iron, the performance was extended by a factor of 5 to 10 using the ceramic materials instead of 440C components. The maximum performance enhancement for the PFPE oils under our test conditions was limited by thermal degradation at the high temperatures generated in the asperity contact region.						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified			
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL	

# PREFACE

The author would like to thank Dr. W. D. Sproul for the TiN coatings and Dr. M. Hilton for the scanning electron microscopy.



Accession For	
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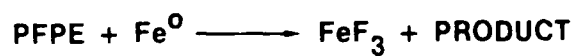
## I. INTRODUCTION

Perfluoropolyalkylether (PFPE) synthetic oils and oil-based greases are relatively new lubricants. They are especially useful in spacecraft because of their low vapor pressure, high viscosity index, and general chemical inertness. However, the usefulness of PFPE lubricants is limited by their poor performance under boundary lubrication conditions [1,2].

In our laboratory, we have studied the degradation of PFPE oils under boundary conditions. We have demonstrated that, in the spacecraft orbital environment, i.e., low partial pressures of oxygen, the oils degrade at high temperatures by reaction with iron (III) fluoride, a Lewis acid catalyst [3]. The degradation reaction is measurable at 350°C, which is 30°C below the temperature where thermal degradation becomes important. Temperatures  $\geq 350^\circ\text{C}$  are estimated to be generated at asperity contacts [4]. The degradation results in the production of acid fluoride chain-cleavage products and a reduction in the average molecular weight of the oil. Furthermore, using surface spectroscopic techniques, we have observed iron fluoride compounds on the wear surfaces after bearing testing [5]. These results support the hypothesis that the PFPE oils interact with the iron in ball-bearing steels at asperity contact temperatures to produce iron (III) fluoride, which further degrades the PFPE through an autocatalytic pathway [1-3,5]. (The scheme for PFPE degradation is given in Fig. 1.) To extend the boundary lubrication performance and usefulness of the PFPE lubricants, the interactions between PFPE and iron metal at the lubricant/steel interface need to be reduced or eliminated.

One method for prolonging wear life under boundary conditions is to use antiwear additives in the oil. Finding appropriate additives for PFPE oils is difficult because of solubility constraints. However, work is currently under way to synthesize additives for PFPE lubricants [6]. An alternative method for prolonging wear life is to use nonferrous materials at the contacting interface, such as ceramic hard-coated or solid ceramic

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STEP 2:

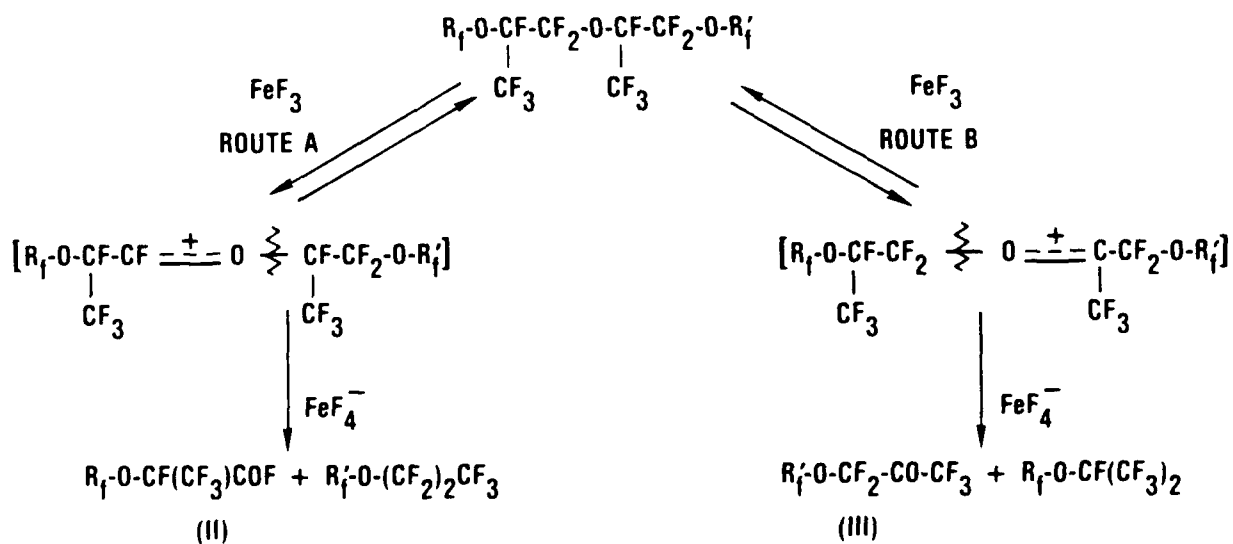


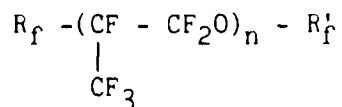
Fig. 1. Hypothesized Mechanism.  
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bearing components. Ceramic hard-coated bearing components have been demonstrated to prolong the lifetime of instrument bearings under elastohydrodynamic (EHD) conditions [7-10]. Solid ceramic bearing components, such as ball bearings with titanium-carbide-coated tungsten-carbide balls and zirconium-nitride-coated raceways, have extended the performance of a linear PFPE oil [11]. Using these nonferrous materials would circumvent the welding interactions in stainless steel components that expose chemically reactive iron metal during the wear process. In this report, we present the results of a series of wear tests using stainless steel, hybrid silicon nitride/stainless steel, and titanium nitride hard-coated stainless steel components with the PFPE oil.

## II. EXPERIMENTAL

### A. MATERIALS

The PFPE fluid, Krytox 143AB, was obtained from E. I. Du Pont Company and was used without further purification. This fluid is a branched compound that can be described by the following generalized formula:



where  $R_f$  and  $R'_f$  are PFPE end groups of unspecified length and  $n$  is approximately 20. The properties of the fluid are given in Table 1.

Aetna F1 thrust ball bearings were used, in which the 4.72 mm (3/16 in.) balls were replaced by grade 10, 440C stainless steel balls (Winsted Precision Ball Company); grade 10, hot-pressed silicon nitride balls (Norton Company); or grade 10, 440C balls that had been reactively sputtered with a 0.75  $\mu$ m TiN hard coating (Basic Industry Research Laboratory, Northwestern University). The thrust bearing raceways were used as received or were hard coated with TiN. The wear disks were 32 mm diam, 440C stainless steel, polished to a mean surface finish of 0.3  $\mu$ m. Wear disks with 0.75  $\mu$ m TiN hard coating were also used.

### B. WEAR-TEST FACILITY

The wear-test facility is shown in Fig. 2 and has been described in detail previously [5]. Boundary lubrication conditions were "forced" by the eccentric interaction between a flat disk, and the balls and lower raceway of a thrust bearing. The eccentricity was produced by noncoaxial alignment of the interacting members: the lower thrust-bearing raceway was positioned ~1 mm off axis. This resulted in a calculated skid/roll ratio of ~0.16. The tests were run at 1750 rpm, which corresponds to a relative linear velocity of 140 m/min. The tests began at ambient temperature; no

Table 1. PFPE Oil Properties

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Viscosity	
37.8°C	85 mm <sup>2</sup> -s <sup>-1</sup>
98.9°C	10.3 mm <sup>2</sup> -s <sup>-1</sup>
Viscosity index	
	113
Pour point	
	-43°C
Density at 23.9°C	
	1.89 x 10 <sup>3</sup> kg-m <sup>-3</sup>
Surface tension at 26°C	
	1.85 x 10 <sup>-2</sup> N-m <sup>-1</sup>
Vapor Pressure	
149°C	40.1 Pa
204°C	334 Pa
260°C	1377 Pa
315°C	7019 Pa

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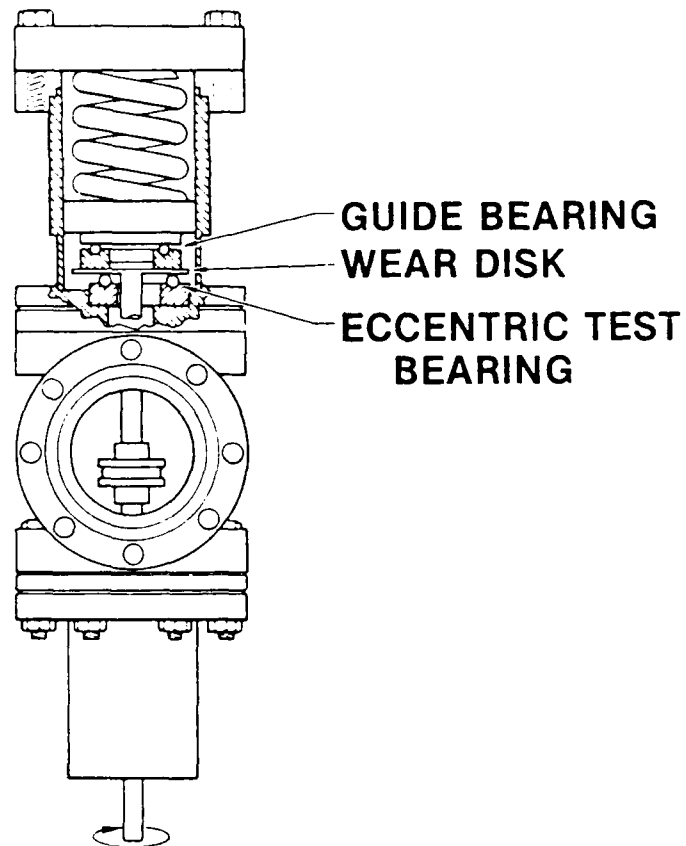


Fig. 2. Wear-Test Fixture.  
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attempt was made to control the temperature. The test conditions are given in Table 2.

The disk/thrust bearing interaction members were housed in a stainless steel vacuum chamber that was pumped with a turbomolecular pump, so that pressures of  $\leq 1.3 \times 10^{-3}$  Pa were routinely achieved, simulating the space environment.

### C. EXPERIMENTAL PROCEDURE

The wear members were lubricated by applying 20  $\mu$ l of a 50% (v/v) solution of the PFPE oil in Freon TF (1,1,2-trichloro-1,2,2-trifluoroethane) to the balls and allowing the solvent to evaporate before placing the wear disk in position. The status of the tests was determined by monitoring the torque indirectly by using the current draw of the motor, measured as the potential drop across a precision 1  $\Omega$  resistor in series with the motor. The torque of the wear members is the difference between the system torque and the torque in the absence of the wear members, which was independently determined. (The torque of the guide bearing was considered to be insignificant.) The tests were terminated when the torque increased to 150% of the initial steady-state value. (This value was arbitrarily chosen to represent system failure.)

Three different materials combinations were used to vary the relative rate of iron metal exposure resulting from wear processes: 440C balls/440C disk;  $\text{Si}_3\text{N}_4$  balls/440C disk; and balls, disk, and raceway hard coated with TiN. These materials combinations would give iron exposure through "welding" interactions, less iron exposure because the welding interaction would be absent, and little or no iron exposure, respectively. (With the exception of the hard-coated combination, the original equipment, a 52100 stainless steel thrust-bearing lower raceway, was used. The Hertzian stress at the ball/raceway interface was much less than that at the ball/disk interface and was considered to be insignificant with respect to lubricant degradation.)

Table 2. Wear Test Conditions

Speed	1750 rpm
Axial load	89-200 N
Pressure	$\sim 1.3 \times 10^{-3}$ Pa
Temperature	ambient <sup>a</sup>
Lubricant quantity	10 $\mu$ l

<sup>a</sup>The temperature was not controlled.

Hertzian stress values were calculated using normal methods. The average stress over the contact area is used in this report [12]. For the TiN hard-coated components, the stress calculation should take into account both the coating and the substrate. However, van der Zwaag and Field [13] have shown that, as the ratio of circular contact radius to coating thickness increases, the calculated Hertzian stress approaches the value calculated from the substrate parameters only. Using Young's modulus values of 640 GPa for TiN [14] and 193 GPa for 440C stainless steel [12], and a radius:thickness ratio of 40, the Hertzian stress for the hard-coated system is within 5% of that calculated for the substrate alone [13]. Because the radius:thickness ratio was  $>40$  for our system, only the substrate parameters were used to calculate the Hertzian stress, with the assumption that the stress of the hard-coated combination was within 5% of the calculated value and would not significantly affect the interpretation of the test results.

### III. RESULTS AND DISCUSSION

The results of the wear tests are given in Table 3. Figure 3 is a plot of wear life as a function of applied axial load. As with wear tests in general, the run-to-run variation in wear life is rather large, which can be seen in the data in Table 3. The values shown are the average of at least three separate runs. In the plotted data, only the average values are shown, with a linear regression fit for each data set shown as a straight line. In spite of the large spread in the wear test values, the trends in the data are clear. The values for  $\text{Si}_3\text{N}_4/440\text{C}$  have essentially the same wear life/load relationship as the values for  $440\text{C}/440\text{C}$ , whereas the values for  $\text{TiN}/\text{TiN}$  are clearly different. For similar applied loads, the  $\text{TiN}/\text{TiN}$  combination results in longer wear lives by a factor of 5 to 10. When plotted as in Fig. 3, the data for the  $\text{Si}_3\text{N}_4/440\text{C}$  combination are presented in "biased" fashion, because the Hertzian stress for this combination is considerably higher than the stress for the  $440\text{C}/440\text{C}$  combination at the same applied load. For engineering considerations, with fixed loads, it makes more sense to use the  $\text{TiN}$  hard coating than the  $\text{Si}_3\text{N}_4/440\text{C}$  hybrid system. However, to understand the chemical processes that occur in the contact region, the Hertzian stress is a more meaningful parameter.

In Fig. 4, the wear-life data for the three materials combinations are plotted as a function of Hertzian stress. The  $\text{TiN}/\text{TiN}$  and  $440\text{C}/440\text{C}$  combinations retain the same relative positions as in Fig. 3, because the Hertzian stress is calculated based on the parameters for the  $440\text{C}$  substrate. However, the  $\text{Si}_3\text{N}_4/440\text{C}$  data are now grouped with the  $\text{TiN}/\text{TiN}$  data, with wear-life values 5-10 times larger than for the  $440\text{C}/440\text{C}$  combination.

Our initial expectation was that the average wear-life values for the  $\text{TiN}/\text{TiN}$  combination would be significantly larger than those for the  $\text{Si}_3\text{N}_4/440\text{C}$  combination. In the latter case, some metallic iron would be

Table 3. Wear Test Results

Applied Load (N)	Hertzian Stress ( $\times 10^9$ Pa)	Average Total Revolutions ( $\times 10^6$ )	Standard Deviation ( $\times 10^6$ )
440C/440C			
134	1.13	2.86	1.47
156	1.21	1.31	1.07
200	1.32	0.397	0.601
$\text{Si}_3\text{N}_4/440\text{C}$			
89	1.14	8.19	3.74
111	1.23	5.86	2.34
134	1.30	2.60	0.60
TiN/TiN			
134	1.13	5.66	3.47
156	1.21	8.91	5.53
200	1.32	3.44	1.15

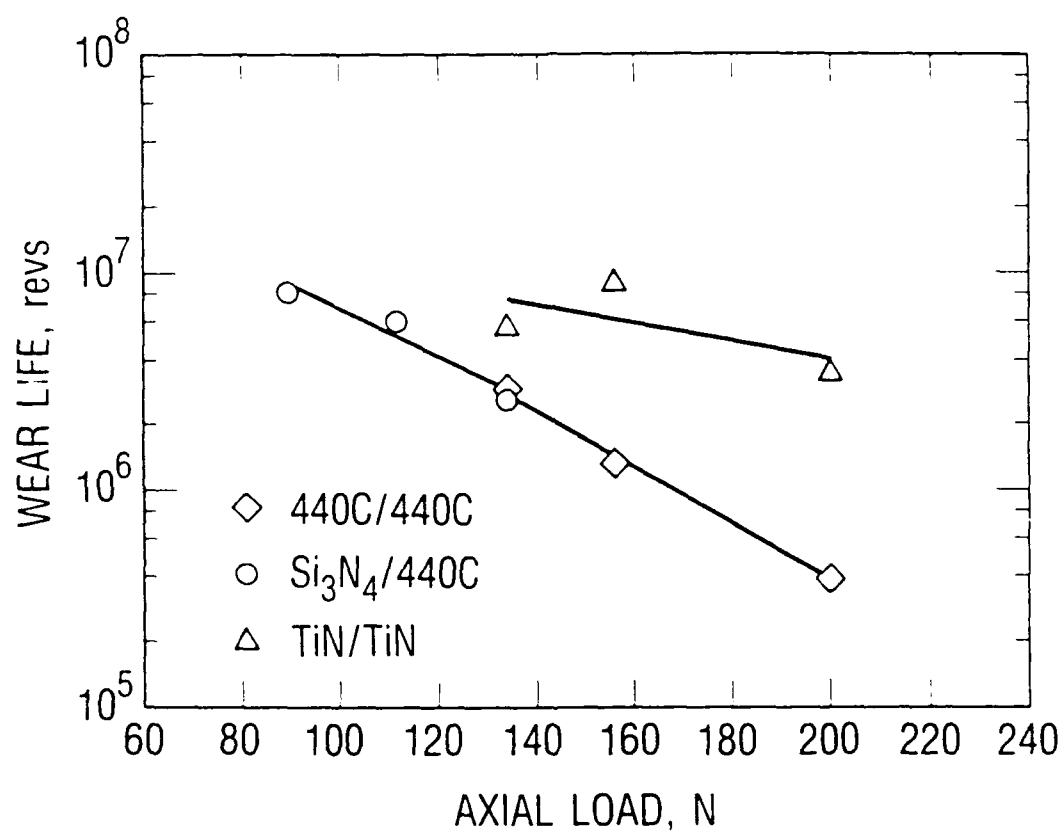


Fig. 3. Wear Life as a Function of Axial Load

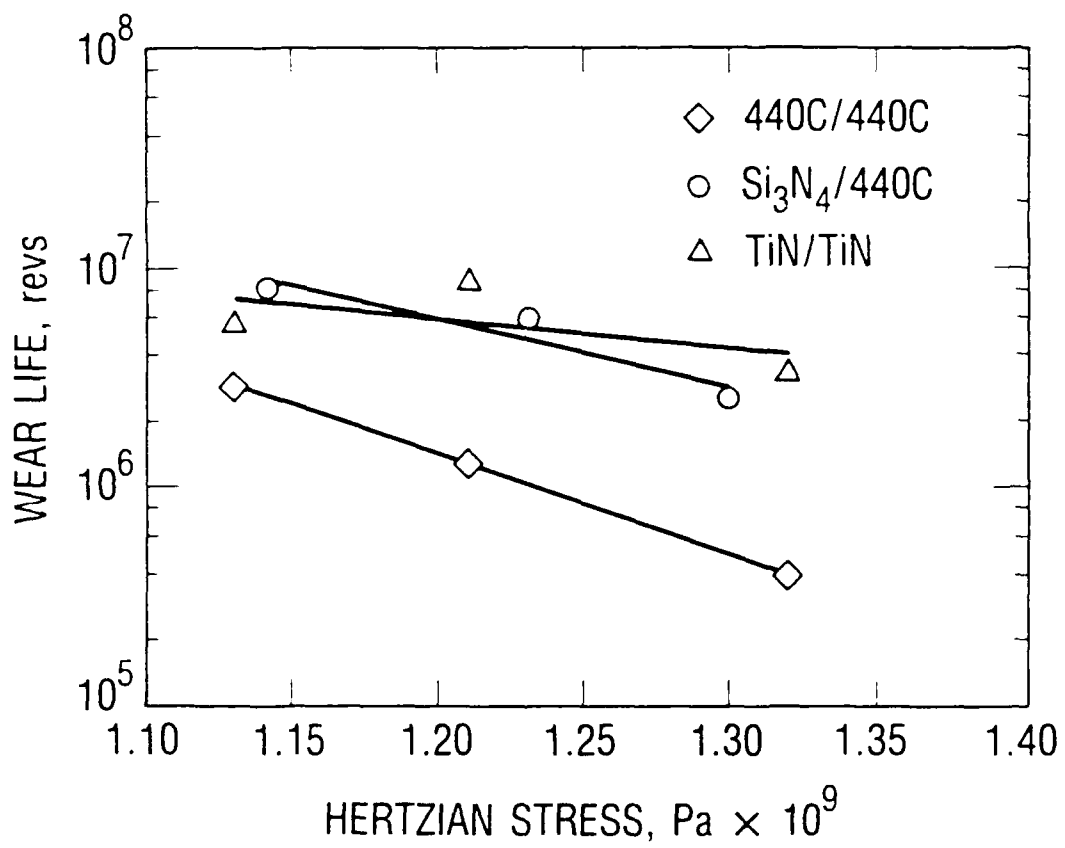


Fig. 4. Wear Life as a Function of Hertzian Stress

expected to be exposed during the wear process (some catalysis), whereas in the former case, no iron metal would be expected (no catalysis). The assumption that the Hertzian stress values for the TiN/TiN system are approximated using substrate parameters would not make a significant difference in the relative wear lives if the approximated values were within 5% of the actual values. We believe that the lack of wear-life enhancement with the TiN/TiN combination over the  $\text{Si}_3\text{N}_4$ /440C combination is the result of a kinetic effect.

In previous work, we had demonstrated that the  $\text{FeF}_3$  catalyzed degradation of the PFPE fluid became kinetically significant at a temperature of  $350^\circ\text{C}$  and that the rate of thermal degradation was not comparable until a temperature of  $380^\circ\text{C}$  was reached [3]. If we assume that the thermal degradation rate doubles for each  $10^\circ\text{C}$  rise in temperature, then at  $350^\circ\text{C}$ , the thermal degradation rate would be slower than the Lewis acid-catalyzed reaction by approximately a factor of 8. (This assumption is used because activation energies, and thus, temperature dependencies, for the catalyzed and thermal degradation reactions are not available.) We conclude that by retarding the acid-catalyzed rate through the elimination or significant reduction in the amount of iron metal formed at the contact, the limiting reaction becomes thermal degradation. To the first order, thermal degradation is not influenced by the choice of materials. [In our investigations, we analyzed the surfaces of the TiN-coated components using scanning electron microscopy (data not shown) and could find no evidence for breakdown of the coating with concomitant exposure of iron.] The implication of this conclusion is that the performance of the PFPE fluids could only be improved by approximately a factor of 8 greater lifetime than that achievable with the 440C/440C system. This predicted enhancement is consistent with the 5-10 lifetime increase measured in our testing.

In addition to the hypothesized mechanism involving Lewis acid-catalyzed PFPE degradation, a mechanism involving reaction of the oxygen in the molecule with iron has also been proposed [11]. Because the interaction with exposed iron is common to both mechanisms, the reduction

of the rate of iron exposure is consistent with longer wear lives in hybrid or coated systems. There is a literature report in which no PFPE lubricant degradation is observed when one of the bearing components is coated with TiC or  $ZrO_2$  [15]. This is in contrast to our findings, in which lubricant degradation is life limiting, even with all the wear components coated with TiN. However, in our findings, the lubricant degradation mechanism for the coated components is believed to be thermal as opposed to catalytic. The observed differences may be the result of differences in the testing. In our test, the lubricant was exposed to rather severe tribological conditions. Antiwear additives, once they are developed for the PFPE fluids, would be expected to further enhance performance by lowering contact temperatures, resulting in a reduction in the rates of catalytic and thermal degradation. This is a topic for further research.

#### IV. CONCLUSIONS

The results of our testing lead to the following conclusions.

1. The performance of PFPE fluids under boundary lubrication conditions can be extended through the use of ceramic or hard-coated components instead of stainless steel.
2. The amount of improvement in wear life appears to be limited by the onset of thermal degradation, which is material independent. In our apparatus, the maximum improvement was approximately a factor of 10.

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